CHEMISTRY OF SOLID PROPELLANT COMBUSTION STUDIED BY MASS SPECTROMETRY AND MODELLING.

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ABSTRACT

The flame structure of composite systems containing ammonium perchlorate with particle size < 50 μm and carboxy-terminated polybutadiene binder, component ratio close to stoichiometric (84% AP - 16% CTPB), was studied at a pressure of $8 \cdot 10^3$ Pa using the method of mass-spectrometric probing. The temperature and concentration profiles of 17 stable flame components were determined. Theoretical modelling of this flame structure was carried out by solving the differential equations describing a reacting multicomponent gas flow, involving heat and mass transfer as well as the kinetic mechanism, including 58 elementary steps and 35 components. Satisfactory agreement was achieved between the experimental and calculated data on concentration profiles of most of the 17 stable components and temperature. Rate constants of some little-studied or unstudied steps were estimated. The data obtained may be used to develop a model of the combustion of solid propellants based on ammonium perchlorate.

INTRODUCTION

The study of combustion mechanism at a molecular level is one of the most important problems of the combustion theory of condensed systems (CS). The experimental results on flame structure give the main information about the combustion chemistry, i.e., the kinetics and mechanism of chemical reactions in the combustion wave.

Earlier we have formulated and followed an approach to the study of the combustion chemistry of condensed systems (CS) which combines (a) experimental study of CS flame chemical structure by mass-spectrometric probing with (b) theoretical modelling of this structure by solving equations, describing the reacting multicomponent gas flow, and taking account of the multistep kinetic mechanism.[1-4] This approach has successfully been used to study the combustion chemistry of AP and RDX,[4] which made it possible to determine the most significant elementary steps and to estimate the rate constants of some little-studied or unstudied steps. In Reference 5, the above approach was employed to study the combustion chemistry of a homogenized composite solid propellant (CSP), containing ammonium perchlorate (AP) and polybutadiene binder with carboxy-terminated polybutadiene (CTPB) in a 77% AP-23% CTPB ratio of the components (thereafter, this composition will be referred to as composition No. 1) at $6 \cdot 10^4$ Pa. The aim of the present paper is to extend these studies. The experimental results are proposed for the flame structure of homogenized composite systems which are close to the stoichiometric ones.

EXPERIMENTAL

Experiments on flame structure were carried out at subatmospheric pressures ($8 \cdot 10^3$ Pa) in a helium flow by methods of mass-spectrometric probing of CS flames described in References 1, 2, and 5. The experiments consist of the following: a burning strand of solid fuel is moved toward the probe at a rate exceeding the burning rate, so that the probe is continuously sampling the gaseous species from all the zones including that adjacent to the burning surface. The sample is transported to the ion source of a time-of-flight mass spectrometer. Mass spectra of the sample are recorded with simultaneous filming of the probe and burning surface. The data allow us to identify stable components and to determine their concentrations and spatial distributions, i.e., the flame microstructure.

Apparata of two types have been developed for studying flame structure. In the first type (which was used in this work), a sample is transported to the ion source as a molecular flow. In the second type, the sample is transported to the ion source as a molecular beam.[4] A quartz cone (exterior and interior angles of 20° and 40-45°, respectively) with an orifice diameter of 20 μm was used as a

probe; the outer tip diameter was 0.3 mm. The thermal flame structure was studied with the help of microthermocouples (SiO_2-coated platinum and platinum-rhodium wires, 0.02 mm in diameter, and tungsten-rhodium wires, 0.02 mm in diameter) embedded in the propellant samples. A composition of 84% AP (particle size <50 µm) and 16% CTPB (composition No. 2) was used. The sample density was 1.5 g/cm, length - 15 mm, diameter - 8 mm. Cigarette paper served as armoured protection. The burning rate was 0.33 mm/s.
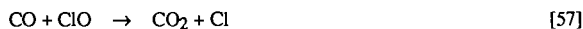
RESULTS AND DISCUSSION

Seventeen stable components (HCl, H_2O, CO, NH_3, CO_2, HClO, NO, O_2, H_2, NO_2, N_2, C_4H_6, C_2H_2, ClO_2, $HClO_4$, Cl_2, HCN) have been detected using mass-spectrometric probing. Concentration profiles of components in the flame were determined from the experimental data. As a rule, the sensitivity coefficients were estimated from the results of inlet system calibration against individual components. In some cases the mass spectra of combustion product samples and the balance equations for elements were used to determine the HCN and H_2O sensitivity coeffecients.

Dots in Fig. 1 (a,b) denote the experimental results from the flame structure, i.e. the dependences of component concentrations and of temperature in the flame under study, plotted as functions of the distance to the burning surface. The data show that the products of CTBP decomposition (C_4H_6, NH_3) are oxidized by those of AP dissociation and decomposition (ClO_2, $HClO_4$ and HClO) in the 1-mm zone of chemical reactions adjacent to the burning surface. These reactions result in HCl, HCN, C_2H_2, NO, CO, and H_2. The O_2 concentration passes through a maximum; that of Cl_2 decreases monotonically. The ammonia concentration in the combustion products decreases almost to zero, whereas in the combustion products of the fuel-rich composition No. 1, the concentration of ammonia was about 3%.

In Fig. 1(a,b), the solid lines represent the results of flame structure modelling using a stationary solution for the complete set of Navier-Stokes equations for reacting gas.[4] The experimental values of temperature and component concentrations were used as boundary conditions. In our calculations, we have used an abbreviated kinetic mechanism which involves 58 reversible steps and 35 components (Table 1),[5] which satisfactorily described the flame structure from composition No. 1. This mechanism has been isolated out of a complete one (258 reversible steps, 49 components).

Analysis of the data obtained shows that in the vicinity of the burning surface, the temperature gradient and the combustion zone width are especially sensitive to variations in the reaction rate constants of the following reactions:

$$NH_2 + O_2 \quad \rightarrow \quad HNO + OH \qquad\qquad\qquad [15]$$

$$CO + ClO \quad \rightarrow \quad CO_2 + Cl \qquad\qquad\qquad [57]$$

$$CO + ClO_2 \quad \rightarrow \quad CO_2 + ClO \qquad\qquad\qquad [58]$$

The most important step is the branching reaction 15. This reaction was studied experimentally in a number of papers, and its rate constant is most often taken from the paper by Dean.[6] However, to reach an agreement between experiment and theory, a rate constant that is 30-times higher must be used. In his recent paper, Dean[7] proposed another way:

$$NH_2 + O_2 \quad \rightarrow \quad NH_2O + O$$
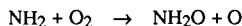
with the rate constant close to our value. There is a satisfactory agreement between experimental and calculated results of the flame structure under investigation. A better agreement with experiment can be achieved by increasing the rate constants for reactions 41 and 58 (see the Table) by 3 and 5 times. Note that the preexponential factors of these reactions are about 10 times as large as those of the same reactions used to calculate the flame structure of the composition No. 1 (with the equal rate constant of the other steps). In order to describe the experimental data on the flame structure of the different composition at various pressures, the mechanism presented in the Table should be improved. Having analyzed the data obtained, we can propose a scheme (Fig. 2) for the transformations of the main initial components (NH_3, C_4H_6, $HClO_4$, ClO_2) resulting from the reaction of oxidizer and fuel in the condensed phase in the AP-CTPB flame. This simplified scheme allows one to understand the main features of the chemical processes in the flame under consideration.

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Table 1. Rate coefficients in form $k_f = AT^b exp(-E/RT)$, Ref. 5. Units are mol, cm^3, sec, K and cal/mol.

No.	Reaction	A	b	E
1.	$HClO_4 \rightarrow ClO_3 + OH$	1.00E+11	0.0	39100
2	$HClO_4 + HNO \rightarrow ClO_3 + NO + H_2O$	3.00E+13	0.0	6000
3	$HClO_4 + HCO \rightarrow ClO_3 + CO + H_2O$	5.00E+13	0.0	0
4	$HClO_4 + HCO \rightarrow ClO_2 + CO_2 + H_2O$	1.50E+12	0.0	0
5.	$ClO_3 \rightarrow ClO + O_2$	1.70E+12	0.5	0
6.	$Cl + O_2 + M \rightarrow ClO_2 + M$	6.00E+11	0.0	11200
7.	$ClO + NO \rightarrow Cl + NO_2$	6.80E+12	0.0	311
8.	$ClOH + ClO \rightarrow Cl_2 + HO_2$	1.00E+14	0.0	10000
9.	$ClOH + OH \rightarrow ClO + H_2O$	1.80E+13	0.0	0
10.	$HCl + OH \rightarrow Cl + H_2O$	5.00E+11	0.0	750
11.	$Cl_2 + H \rightarrow HCl + Cl$	8.40E+13	0.0	1150
12.	$NH_3 + ClO \rightarrow NH_2 + ClOH$	4.24E+11	0.5	6400
13.	$NH_3 + Cl \rightarrow NH_2 + HCl$	4.50E+11	0.5	100
14.	$NH_3 + OH \rightarrow NH_2 + H_2O$	1.00E+11	0.68	1100
15.	$NH_2 + O_2 \rightarrow HNO + OH$	6.00E+9	0.5	0
16.	$NH_2 + NO \rightarrow N_2 + H_2O$	2.40E+11	0.0	0
17.	$NH_2 + NO \rightarrow N_2H + OH$	6.00E+11	0.0	0
18.	$N_2H + NO \rightarrow HNO + N_2$	5.00E+13	0.0	0
19.	$HNO + OH \rightarrow NO + H_2O$	3.60E+13	0.0	0
20.	$HNO + O_2 \rightarrow NO_2 + OH$	1.00E+13	0.0	10000
21.	$HNO + H \rightarrow H_2 + NO$	1.00E+12	0.5	900
22.	$NO + H + M \rightarrow HNO + M$	3.20E+15	0.0	-600
23.	$N_2 + HO_2 \rightarrow HNO + NO$	8.00E+10	0.5	41800
24.	$NO + HO_2 \rightarrow NO_2 + OH$	3.00E+12	0.5	1800

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25.	$NO_2 + H$	$\rightarrow$	$NO + OH$	5.00E+14	0.0	1740
26.	$H_2 + OH$	$\rightarrow$	$H_2O + H$	1.00E+8	1.6	3290
27.	$C_4H_6 + OH$	$\rightarrow$	$n\text{-}C_4H_5 + H_2O$	5.00E+12	0.68	1100
28.	$C_4H_6 + OH$	$\rightarrow$	$i\text{-}C_4H_5 + H_2O$	5.00E+12	0.68	1100
29.	$C_4H_6 + ClO$	$\rightarrow$	$n\text{-}C_4H_5 + ClOH$	5.00E+12	0.5	6400
30.	$C_4H_6 + ClO$	$\rightarrow$	$i\text{-}C_4H_5 + ClOH$	5.00E+12	0.5	6400
31.	$C_4H_6 + Cl$	$\rightarrow$	$n\text{-}C_4H_5 + HCl$	6.75E+12	0.5	100
32.	$C_4H_6 + Cl$	$\rightarrow$	$i\text{-}C_4H_5 + HCl$	2.25E+11	0.5	100
33.	$i\text{-}C_4H_5 + M$	$\rightarrow$	$n\text{-}C_4H_5 + M$	1.00E+14	0.0	6500
34.	$n\text{-}C_4H_5$	$\rightarrow$	$C_4H_4 + H$	5.00E+14	0.0	45700
35.	$i\text{-}C_4H_5$	$\rightarrow$	$C_4H_4 + H$	6.30E+15	0.0	58700
36.	$n\text{-}C_4H_5$	$\rightarrow$	$C_2H_2 + C_2H_3$	5.00E+13	0.0	40000
37.	$i\text{-}C_4H_5$	$\rightarrow$	$C_2H_3 + C_2H_2$	6.30E+10	0.0	32000
38.	$i\text{-}C_4H_5 + Cl$	$\rightarrow$	$C_4H_4 + HCl$	1.00E+14	0.0	1000
39.	$i\text{-}C_4H_5 + ClO$	$\rightarrow$	$C_4H_4 + ClOH$	1.00E+14	0.0	1000
40.	$C_4H_4 + H$	$\rightarrow$	$C_2H_3 + C_2H_2$	1.30E+14	0.0	1380
41.	$C_4H_4 + NO_2$	$\rightarrow$	$CH_2 + HCN + HCO$	5.00E+13	0.0	0
42.	$C_2H_2 + C_2H_2$	$\rightarrow$	C_4H_4	5.90E+12	0.0	44600
43.	$CH_2CO + OH$	$\rightarrow$	$CH_2O + HCO$	2.82E+13	0.0	0
44.	$CH_2OO + NO_2$	$\rightarrow$	$CH_2O + CO + NO$	1.00E+13	0.0	6000
45.	$C_2H_3 + O_2$	$\rightarrow$	$CH_2O + HCO$	6.00E+13	0.0	0
46.	$C_2H_2 + H$	$\rightarrow$	C_2H_3	5.50E+12	0.0	2330
47.	$C_2H_2 + OH$	$\rightarrow$	$CH_3 + CO$	2.00E+12	0.0	7000
48.	$CH_2O + M$	$\rightarrow$	$CO + H_2 + M$	2.50E+15	0.0	28600
49.	$CH_4 + Cl$	$\rightarrow$	$CH_3 + HCl$	2.50E+13	0.0	3830
50.	$CH_4 + ClO$	$\rightarrow$	$CH_3 + ClOH$	6.00E+11	0.5	5700
51.	$CH_4 + H$	$\rightarrow$	$CH_3 + H_2$	2.20E+4	3.0	8520
52.	$CH_4 + OH$	$\rightarrow$	$CH_3 + H_2O$	1.60E+6	2.1	2460
53.	$CH_3 + H$	$\rightarrow$	CH_4	6.00E+16	-1.0	0
54.	$HCO + M$	$\rightarrow$	$CO + H + M$	2.50E+14	0.0	16800
55.	$HCN + OH$	$\rightarrow$	$NH_2 + CO$	2.00E+11	0.0	0
56.	$CO + OH$	$\rightarrow$	$CO_2 + H$	4.40E+6	1.5	-740
57.	$CO + ClO$	$\rightarrow$	$CO_2 + Cl$	3.00E+12	0.0	1000
58.	$CO + ClO_2$	$\rightarrow$	$CO_2 + ClO$	5.00E+10	0.0	0
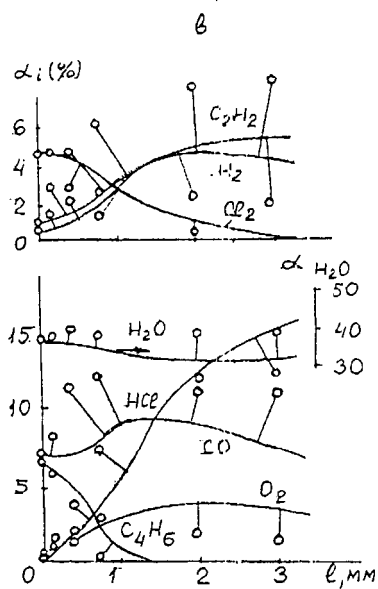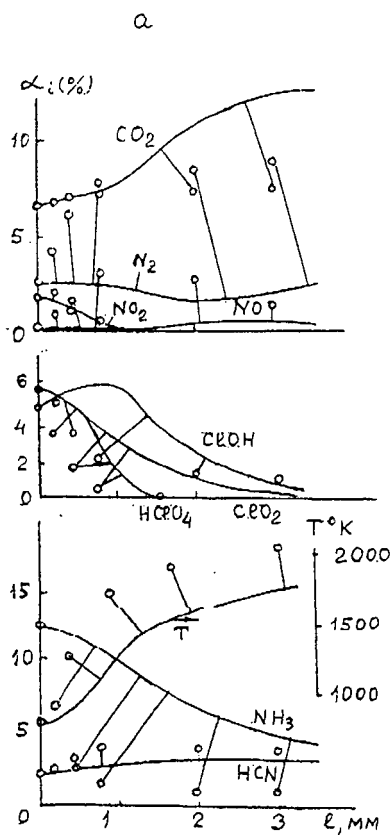
Fig. 1a, b. Temperature and concentrations of stable components in the studied flame vs distance to the burning surface: dots – experiment; solid lines – calculation.
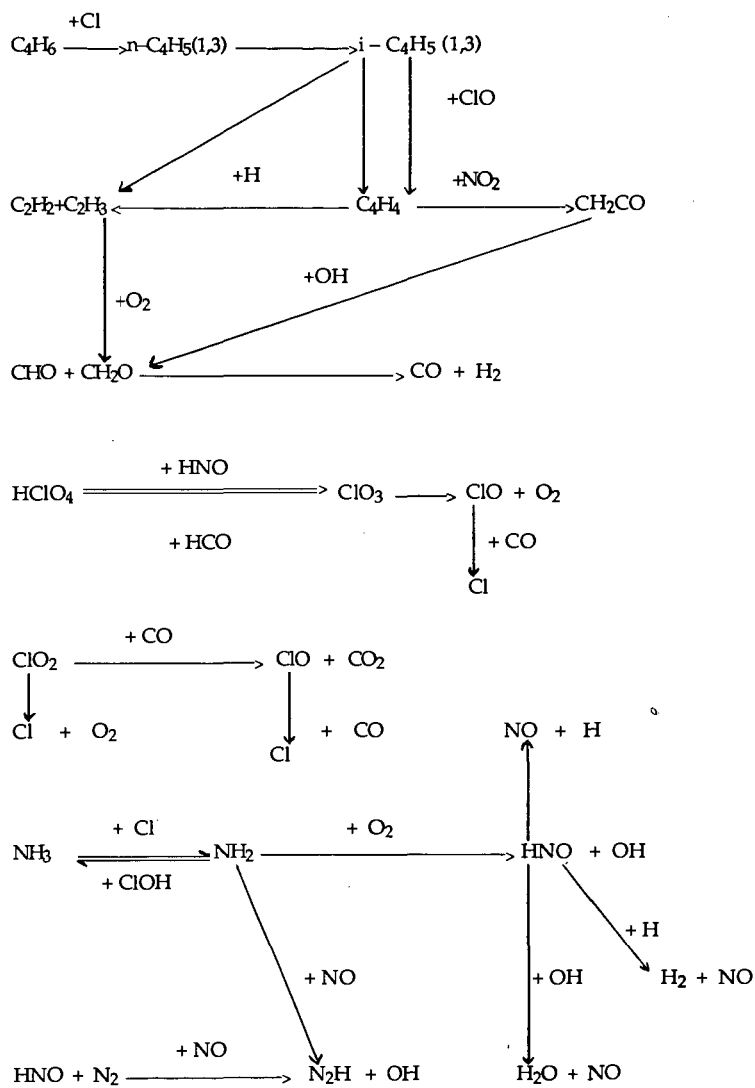
1586

C₄H₆ —(+Cl)→ n–C₄H₅(1,3) ——→ i – C₄H₅ (1,3)

(Figure scheme - chemical transformations)

$$C_4H_6 \xrightarrow{+Cl} n\text{-}C_4H_5(1,3) \longrightarrow i-C_4H_5\,(1,3)$$

$+ClO$

$+H$ $+NO_2$

$C_2H_2+C_2H_3 \longleftarrow C_4H_4 \longrightarrow CH_2CO$

$+OH$

$+O_2$

$CHO + CH_2O \longrightarrow CO + H_2$

$$HClO_4 \xrightarrow{+ HNO} ClO_3 \longrightarrow ClO + O_2$$

$+ HCO$ $+ CO$

Cl

$+ CO$

$ClO_2 \longrightarrow ClO + CO_2$

$Cl + O_2$ $+ CO$

Cl

$NO + H$

$+ Cl$ $+ O_2$

$NH_3 \rightleftarrows NH_2 \longrightarrow HNO + OH$

$+ ClOH$

$+ H$

$+ NO$ $+ OH$ $H_2 + NO$

$+ NO$

$HNO + N_2 \longrightarrow N_2H + OH$ $H_2O + NO$

Fig. 2. A scheme of chemical transformations in the AP – CTPB flame.

1587